

Provided for non-commercial research and education use.  
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

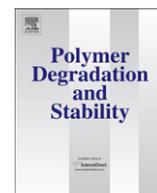
In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at SciVerse ScienceDirect

## Polymer Degradation and Stability

journal homepage: [www.elsevier.com/locate/polydegstab](http://www.elsevier.com/locate/polydegstab)

# Hydration-induced reinforcement of rigid polyurethane–cement foams: The effect of the co-continuous morphology on the thermal-oxidative stability

Letizia Verdolotti<sup>a,c</sup>, Marino Lavorgna<sup>a,c,\*</sup>, Ernesto Di Maio<sup>b,c</sup>, Salvatore Iannace<sup>a,c</sup><sup>a</sup> Institute for Composite and Biomedical Materials, National Research Council (IMCB-CNR), P.le Tecchio 80, 80125 Naples, Italy<sup>b</sup> Department of Materials and Production Engineering, University of Naples Federico II, P.le Tecchio 80, 80125 Naples, Italy<sup>c</sup> Hycucem s.r.l. P.le E.Fermi, 1, Loc Granatello Portici, Naples, Italy

### ARTICLE INFO

#### Article history:

Received 31 July 2012

Received in revised form

25 October 2012

Accepted 31 October 2012

Available online 7 November 2012

#### Keywords:

HIRP–C

Hydrated cement

Polyurethane foam

Co-continuity

Thermal properties

Fire resistance

### ABSTRACT

The flame retardancy of a new composite polyurethane–cement foams based on the innovative concept of “Hydration-Induced Reinforcement of Polyurethane Rigid Foams”, HIRP–C, through the formation of an organic–inorganic co-continuous morphology have been investigated. The hybrid foams were prepared by allowing polyether polyol mixed with catalysts, surfactants and cement (up to final weight of 60 wt%) to react with Metylen-Diphenyl-Diisocyanate without flame retardant. The composite foams were then cured at 60 °C in water for 72 h in order to hydrate the anhydrous cement particles. The hydrated cement phases engender a co-continuous structure within the polyurethane matrix. For comparison both neat polyurethane foams and flame retardant filled foams were also prepared. The composite and the hybrid foams were characterized by X-ray diffraction, mechanical compressive testing and the scanning electron microscopy, while the thermal-oxidative properties were characterized by thermogravimetric analysis. Cone calorimeter analysis which allowed to determine the key properties of thermal degradation, namely the heat release rate, the smoke and CO production from foam combustion. The hybrid foams exhibit a significant improvement of mechanical properties due to the hydration of the cement particles as compared to the un-hydrated composite foam. The results of the thermal characterization showed that the presence of the amounts of inorganic cement particles, alongside with the formation of a co-continuous morphology, produces enhancements of fire behavior and improvements in the thermal-oxidative stability of polyurethane. The flame retardancy who essentially due to the physical action of the inorganic phase which constitutes a barrier at the surface and opposes to the diffusion of volatiles and oxygen.

© 2012 Elsevier Ltd. All rights reserved.

## 1. Introduction

Polyurethanes (PUR) foams, with rigid and flexible cellular structure, are widely used as thermal and acoustic insulator especially in building, household and automotive. In these fields, the enhancement of the fire resistance properties of foamed products is of paramount importance and that is still more mandatory for PUR, since polyurethane is a highly flammable and combustible material [1–3]. Depending on the chemical structure of polyols and isocyanates, as well as the isocyanurate index and the foam density, the PUR can be thermally stable in the range 200–300 °C. At higher temperature they start to decompose with mechanisms depending on the boundary conditions [4]. In particular, in an inert

environment the PUR foams decompose through the cleavage of the urethane bonds in polyols and isocyanates, followed by the dissociation of urethane cycles to amine and carbon dioxide. In oxidative conditions the decomposition of PUR foams is more complicated, due to simultaneous chain scissions, crosslinking, oxidation and gas evolution. In addition, the burning of PUR foams evolves through the formation of gaseous isocyanates, which can then re-polymerize in the gas phase and condense as “yellow smoke”. Generally, this process is accompanied by liquid polyols pool, which continues to decompose to form heat, CO and CO<sub>2</sub> gases [5].

The improvement of thermal and fire performances of PUR foams by means of flame retardants and inorganic fillers, or chemical modification by introducing isocyanurate rings or carbodiimides has been investigated and the results have been thoroughly summarized by Singh in a recent review [6]. For instance, the flame retardants incorporated in the polymeric matrix, act both in the condensed phase and in the vapor phase or simultaneously in

\* Corresponding author. IMCB-CNR, P.le Tecchio 80, 80125 Naples, Italy. Tel.: +39 081 775 8838; fax: +39 081 775 8850.

E-mail address: [mlavorgn@unina.it](mailto:mlavorgn@unina.it) (M. Lavorgna).

both phases through chemical and/or physical mechanisms, interfering with the combustion process during heating, pyrolysis, ignition or flame spread. The main flame-retardant compounds used in the stabilization of PUR foams belong to the following classes [6]: (1) organic compounds (i.e. halogenated compounds), that act mostly in the vapor phase by a radical mechanism, to interrupt the exothermic processes and to hinder combustion through the suppression of radicals. This is, usually, accompanied by the generation of toxic compounds (furans, dioxins) during the combustion [7]; (2) inorganic phosphorous and phosphorous containing compounds, which act mainly as char-forming agents reducing generation of flammable gases [8], (3) Silicon containing additives, which promote the formation of a high quantity of char residue converted into a continuous silica layer during oxidation; (4) inorganic compounds (metal hydroxides, such as aluminum trihydrate-ATH), that, during the combustion, are subjected to an endothermic decomposition mechanism, releasing water and oxides with low emission of smoke. However, some of these compounds exhibit a relatively low flame-retardant efficiency and thermal stability and lead to an extensive deterioration of the physical/mechanical properties of the polymers they are added to [7].

In this context, the technological and scientific research is focused on the investigation on new “environmentally friendly” flame retardants able to reduce or to avoid the fire threats in the PUR foamed systems. Alongside the use of conventional flame retardants, the dispersion of nanometric particles as layered, fibrous and particulate materials has been known to contribute to the enhancement of thermal and fire resistance of polymeric matrixes [9]. Layered particles (i.e. nanoclays) in the flexible PUR foams create a protective barrier that limits heat transfer into the material during the combustion and inhibits volatile diffusion. This behavior is ascribed mainly to the migration of the clay nanolayers to the surface of the nanocomposite as well as the formation of protonic catalytic sites onto the clay surface that catalyze the creation of a stable char residue during the combustion [10]. Seo et al. [11] reported that the fire resistance of PUR foams filled with nanoclay is mainly governed by the dispersion of filler, optimized when the filler is homogeneously dispersed in isocyanate by means of ultrasound treatments. Mahfuz et al. [12] reported the enhancement of thermal stability of PUR foams through the use of SiC and TiO<sub>2</sub> particles, which probably contributed to the increase of the crosslinking and the density of the foams. Gilman [13] and Zammarano et al. [14] reported that the use of carbon nanotubes (CNTs) is effective in lowering the peak of heat release rate by 35% in polyurethane flexible foams. The main reason being the formation of a CNTs percolative network that makes the melt behave as a gel, therefore inhibiting dripping and incrementing the heat shielding effect.

As widely described by Laoutid et al. [9], however, most of nanocomposites still burn with very little, if any, reduction in the total heat release and as well as any increment of the time to ignition. Some interesting advantages in terms of improvement of fire properties and thermal stability [15] of polymeric systems can be obtained by using, simultaneously, both nanoparticles and flame retardants or nanoparticles with different aspect ratios. Modesti et al. [16] investigated the synergistic effect on fire resistance of PUR foams of phosphorous based flame retardant and layered silicate. The results showed that, during burning, the clays constituted a barrier at the surface of the sample, being, in turn, effective in the slowing down the diffusion of volatiles and oxygen while the phosphinates are more effective in both condensed and gas phases.

Zatorski et al. [17] proved that expandable graphite is able to form a barrier for oxygen and volatile gases and also nanoparticles, such as nanoclays and nanosilica, where used in combination with

halogen containing fire retardants with a significant reduction of flammability in polyurethane–polyisocyanurate foams. Finally, polyurethane rigid foams containing fly ash and intumescent flame retardants exhibited a significant enhancement in the fire resistance and thermal stability due, mainly, to the formation of a tough char layer, which in turn protects the underlying materials from further burning [5].

Recently, a new class of hybrid materials based on polyurethane foam (flexible and rigid) and cement powder has been developed, wherein, through a hydration process, the co-continuity between the organic and inorganic phases is obtained. In these materials, defined as “Hydration-Induced Reinforcement of Polyurethane–Cement” (HIRP–C) hybrid foams, the presence of co-continuous morphology induced an enhancement of mechanical and functional properties, since polyurethane matrix and hydrated inorganic phases may cooperate intimately and synergistically to improve the performances of the resulting material [18–20].

The aim of this paper is to study the effects of the co-continuous organic–inorganic morphology on the thermal-oxidative stability and fire resistance of HIRP–C foams, by means of cone calorimeter testing and thermogravimetric analysis. The fire behavior of hybrid foams has been compared to that of neat polyurethane foams and polyurethane foams filled with a conventional flame retardant. The mechanical and morphological analyses were also used to assess the effective improvement brought about by the formation of co-continuous structure.

## 2. Experimental

### 2.1. Materials

Polyol polyether and Metylen-Diphenyl-Diisocyanate (MDI) were kindly supplied by Huntsman Tioxide Europe (Ternate, Italy); catalysts, chain extenders, silicone surfactant, flame retardant (Tris(1-chloro-2-propyl)phosphate, TCPP) were supplied by Momentive Performance Materials (Germany). Portland cement in powder form, CEM type IIA-S class 42,5R was used. The chemicals were used as received. Distilled water was utilized as chemical blowing agent.

### 2.2. Methods

#### 2.2.1. Samples preparation

Composite cement–polyurethane foams with density of 300 kg/m<sup>3</sup> were prepared by mixing at room temperature the inorganic cement powder (60 wt% with density equal to 3300 kg/m<sup>3</sup>) to the polyurethane precursors, namely MDI, polyol with catalysts, silicone surfactant and chain extenders (40 wt%). More details about the preparation of both un-hydrated polyurethane–cement foams (named P–C, with density equal to 300 kg/m<sup>3</sup>) and hydrated polyurethane–cement foams (named HIRP–C, with density of 320 kg/m<sup>3</sup> for an amount of chemically bonded water of hydrated sample ranging 12–17 wt%) were reported in previous papers [18–20]. Neat polyurethane formulation (e.g. without cement: neat-PUR, with density of 120 kg/m<sup>3</sup>) was also produced for proper comparison. Moreover, in order to assess the effect of co-continuity on the flammability and fire properties of HIRP–C foams, polyurethane foams filled with 10 wt% of TCPP flame retardant was also synthesized. This material, named as PUR-FR, was produced with a density equal to 150 kg/m<sup>3</sup>.

#### 2.2.2. X-ray diffraction

The mineralogical composition of composite foams has been investigated by X-ray diffraction (XRD). The samples were milled at room temperature and then characterized by using a Philips

diffractometer equipped with a Philips X-ray generator, type PW1710 (Philips, Holland). The X-ray beam was nickel-filtered Cu K $\alpha$  radiation of wavelength 1.54 Å operated at the generator voltage of 40 kV and current of 20 mA. The diffraction patterns were collected automatically at a scanning rate of 0.6°/min with 0.01°/s steps.

### 2.2.3. Micro-structural analysis

The foamed samples were analyzed by scanning electron microscopy (SEM), to investigate the morphology of foam (i.e. size cell and porosity extent) and the formation of hydrated products from cement hydration. An electron microscopy operating at 20 kV, mod. S440 from Leica Microsystems GmbH, (Germany) was used. The samples were first sectioned with a razor blade and then coated with gold using a sputter coater (mod. SC500, Emscope, UK).

### 2.2.4. Mechanical properties

Compressive tests were carried out on a SANS testing machine (mod. CMT4304, Shenzhen SANS Testing Machine Co., China) with a 30 kN load cell, according to ASTM D1621.

### 2.2.5. Thermal properties

Thermogravimetric analysis (TGA) and cone calorimetric characterization were used to investigate the effect of conventional flame retardant (TCPP), anhydrous cement filler (un-hydrated cement) and co-continuous inorganic structure (hydrated cement) on the thermo-oxidative degradation of rigid PUR foams.

**2.2.5.1. Thermogravimetry analysis (TGA/DTG).** The thermal degradation of the produced foams was investigated by thermogravimetric (TGA) and derivative TGA (DTG) analyses only for the first degradation step (160–400 °C). The tests have been carried out on a TGA2950 (TA Instruments, USA) under air atmosphere. The foam samples were heated on platinum pans from 30 °C up to 1000 °C by applying the following heating rates: 5, 10 and 20 °C/min. In order to analyze the effect of the integrity of the inorganic network on thermal-oxidative degradation process, TGA experiments were also performed on foam samples milled to fine powder.

**2.2.5.2. Cone calorimetry analysis.** To analyze the fire reaction exhibited by the several foams in realistic fire conditions, cone calorimetry analysis was performed according to ISO 5660 [21], by using an oxygen consumption cone calorimeter (Fire Testing Technology, FFT dual cone calorimeter model). Specimens of the size of 100 × 100 × 20 mm<sup>3</sup> were exposed in the horizontal orientation to an external heat flux of 50 kW/m<sup>2</sup>, which corresponds to a common heat flux in mild fire scenario [22]. Three samples for each system were investigated. Samples were pre-conditioned to constant mass at a temperature of 23 ± 2 °C and relative humidity 50 ± 5% in accordance with ISO 554 [23].

Several combustion parameters such as time to ignition (TTI, s), heat release rate (HRR, kW/m<sup>2</sup>), peak heat release rate (pHRR, kW/m<sup>2</sup>), fire performance index (which corresponds to the ratio of TTI to pHRR, s<sup>2</sup>m<sup>2</sup>/kW), total heat release (THR, kJ/m<sup>2</sup>), total heat evolved (THE, kJ/m<sup>2</sup>), total mass loss, CO and smoke production were measured according to ISO 5660 [21].

In details, the HRR represents the thermal energy released by a material per unit area when exposed to a fire radiating at constant heat flux. It is measured as the oxygen consumption for the thermo-oxidative degradation of the combustion product stream.

The THR is defined as the time integral of the HRR and represents the total heat output up to that point. The THE is defined as the THR at the end of the cone calorimeter test and it indicates the total amount of heat that can be released during the burning of the material [24]. It is therefore the *fire load* of the specimen in the test

fire scenario. The pHRR represents the peak value of the HRR and it dictates the *flashover* potential in a real fire scenario.

## 3. Results and discussion

### 3.1. X-ray diffraction

X-ray diffraction analysis was performed to verify the extent of cement hydration by monitoring the depletion of anhydrous crystalline minerals of cement [19,20,25,26], which transform in amorphous hydrated calcium silica phase (CSH). The X-ray pattern of anhydrous cement, reported in Fig. 1, shows the presence of crystalline phases identified as calcium carbonate, CaCO<sub>3</sub> at 2 $\theta$  equal to 23° and 29.3°, and anhydrous calcium silicates, 2CaO·SiO<sub>2</sub>(belite) and 3CaO·SiO<sub>2</sub> (alite) at 2 $\theta$  equal to 32°–33°, 34° and 41.5° respectively [26,27]. The anhydrous calcium silicate phases are also detected in the X-ray pattern of the P–C foam, wherein the anhydrous cement is present at 60 wt%. In the X-ray pattern of HIRP–C foam, the intensity of the anhydrous calcium silicate phases decreases as consequence of the hydration process, which leads to the formation of amorphous calcium silicate hydrated phases [19,20,26,27]. Moreover, additional crystalline phases as calcium hydroxide and ettringite (i.e. trisulfoaluminate of calcium hydrated) appear in the X-ray pattern of the HIRP–C arising, respectively, from the hydration of anhydrous silicate phases and the calcium aluminate in presence of gypsum. The results confirm that, during hydration process, the cement hydration effectively takes place. However the complete disappearance of the peaks ascribed to the anhydrous cement phases was not achieved, since the hydrophobic polymer matrix limits the permeation of water through the sample thickness and hinders complete hydration of the cement within the HIRP–C.

### 3.2. Micro-structural analysis

SEM micrographs of the fractured surface of HIRP–C foam are shown in Fig. 2. In particular Fig. 2a shows the typical cellular morphology of closed celled rigid PUR foams, with the hydrated cement located in the struts and on the internal walls, whereas in Fig. 2b and c typical cement hydrated phases identified as ettringite (needlelike crystals, [26]) and calcium silicate hydrate (i.e. gel-like flocks, [26]), can be observed. It is worth noting that as a consequence of the formation of hydrated phases and their reciprocal overlapping, a continuous inorganic network, interconnect with

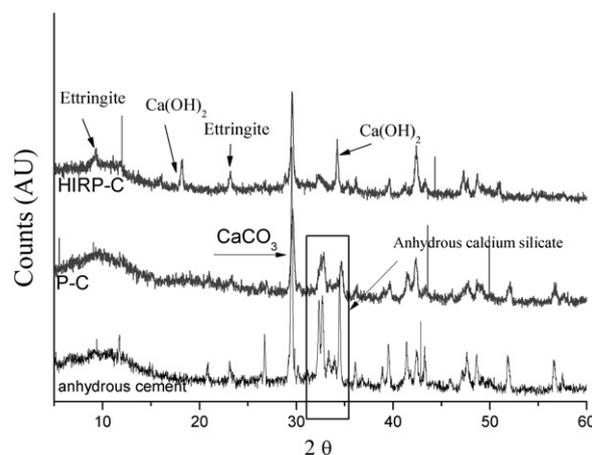


Fig. 1. XRD patterns of anhydrous cement powder and selected P–C and HIRP–C foams.

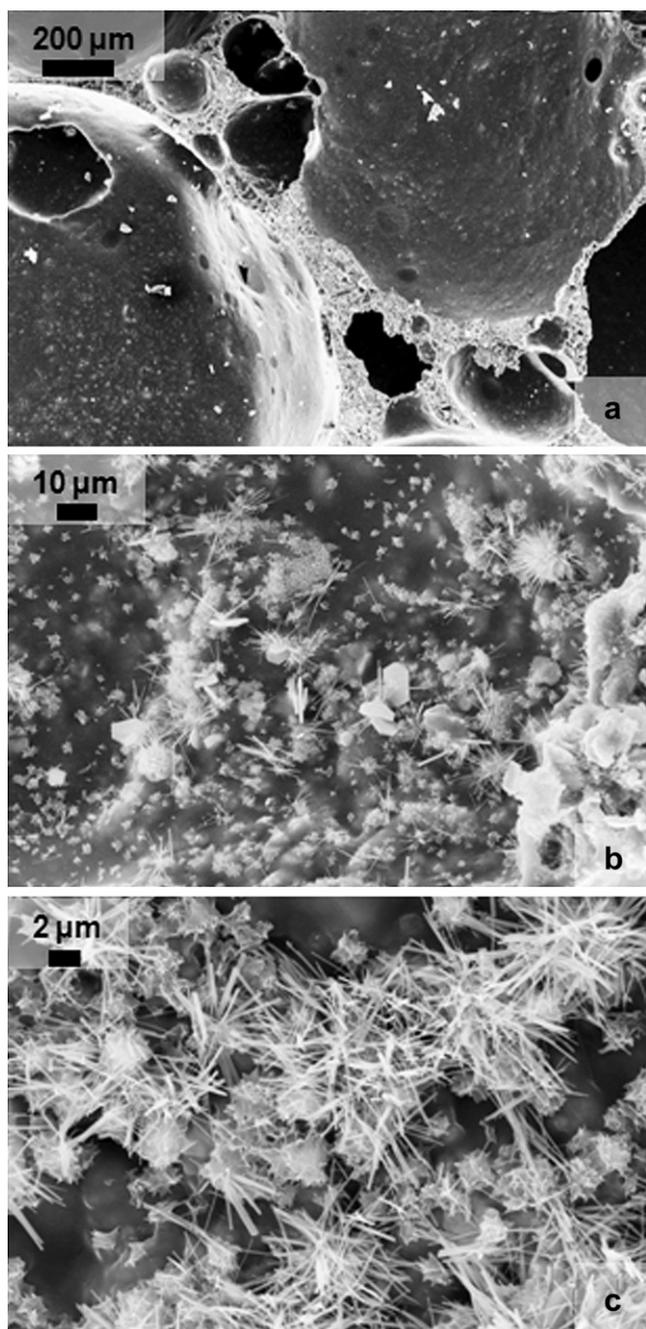


Fig. 2. SEM micrographs of HIRP-C foam sample at different magnification a) Mag: 171 $\times$ , b) Mag: 7.41 k $\times$ , c) Mag: 1.92 k $\times$ .

the PUR network, gave rise to a co-continuous morphology (see Fig. 2c).

### 3.3. Mechanical properties

Fig. 3 reports selected stress–strain ( $\sigma$ – $\epsilon$ ) curves for HIRP-C and P-C samples. It is noted that the hydration of cement filler results in an enhancement of both the stiffness and the strength of HIRP-C foams with respect to P-C. In details, the elastic modulus in compression ( $E$ ) increased from ca. 70–196 MPa, whereas the strength ( $\sigma$ ) increased from 3.1 to 4.31 MPa. As reported in previous papers [19,20,25] the improvement of compressive mechanical properties is a direct consequence of the occurrence of cement

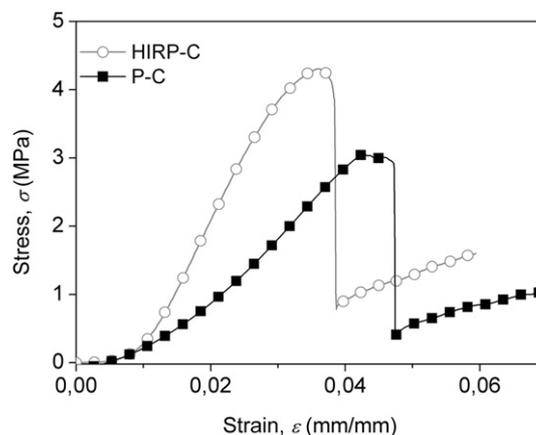


Fig. 3. Stress–strain curves for selected P-C and HIRP-C foams.

hydration and the consequently formation of co-continuity between the organic and inorganic phases.

### 3.4. Thermal properties

#### 3.4.1. Thermogravimetry analysis (TGA/DTG)

TGA thermograms in air flux of neat-PUR, P-C and HIRP-C foams are shown in Fig. 4. The curves at heating rates of 5, 10 and 20 °C/min have been normalized at 180 °C to account for both the chemically bound water (i.e. water present in the chemical structure of cement hydrated phases, both CSH and ettringite, removed by heating in the range 80–140 °C [20]). In the inset, the corresponding derivative thermograms curves of the first degradation step (in the range 200–450 °C) are reported.

From the thermograms of neat-PUR, it is shown that the degradation mechanism occurs through two different steps. The first degradation step occurs in the range 200–450 °C (324 °C is the temperature value at maximum weight loss rate, for heating at 10 °C/min) with both onsets and end-degradation offsets temperatures increasing with the heating rates. The second degradation step occurs in the range 420–700 °C (528 °C is the temperature value at maximum weight loss rate for heating at 10 °C/min) with onsets and end-degradation offsets temperatures still depending on the heating rates. The weight losses are 40 wt% and 60 wt%, respectively, for the first and second degradation step. These losses do not change with the heating rates. According to a recent work from Thirumal et al. [28], the first weight loss stage is ascribed to the breaking of urethane and allophanate links leading to the depolymerization of PUR to monomer precursors such as polyol and isocyanate. In details the isocyanate dimerizes to form carbodiimide, with evolution of volatiles compounds as CO<sub>2</sub>, alcohols, amines, aldehydes, CO, etc. The carbodiimide is stable up to higher temperatures when it degrades, giving rise to the second degradation step.

The thermo-oxidative degradation of P-C and HIRP-C foams was found to occur with a different mechanism; in comparison to neat-PUR foam. During heating three degradation steps are observed. In the literature, it is reported that in silico–aluminate systems (clay, silica, alumina etc.) acid sites on the surface of the filler has a catalytic effect on the PUR degradation, lowering the temperature for the onset of maximum weight loss [29]. In P-C and HIRP-C foams, both the presence of anhydrous cement particles and the co-continuous morphology increase the onset temperature and the temperature at maximum loss degradation rate of the first degradation step with respect to the neat-PUR foam. On the other side, it seems that anhydrous and hydrated cement phases have

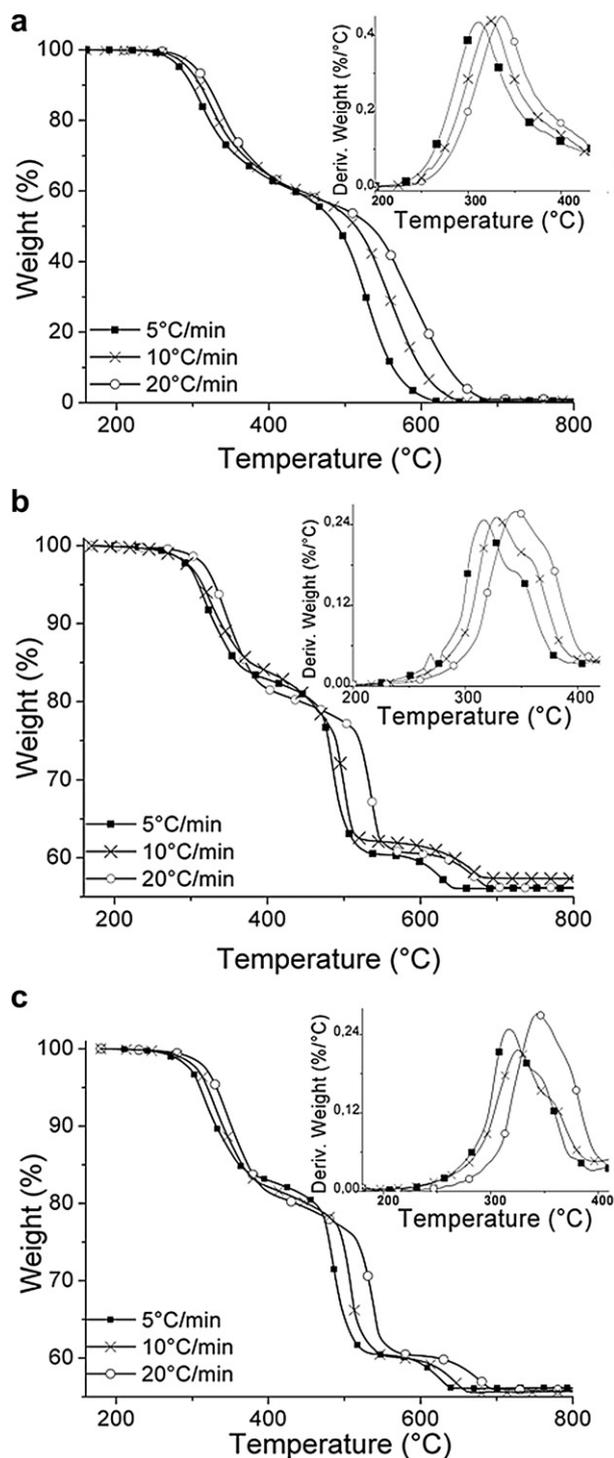


Fig. 4. Thermogravimetric TGA and DTG curves for a) neat-PUR; b) P-C and c) HIRP-C foams in air.

a detrimental effect on the thermal-oxidative stability of the second degradation step.

The mass lost at the end of second degradation stage, which may be ascribed to the degradation of PUR phase is approximately 38 wt% and 40 wt%, respectively, for P-C and HIRP-C foams. This result is in agreement with the compositional weight ratio of organic to inorganic phases (40/60) used for the formulation of composite foams. Furthermore, in the temperature range 200–550 °C, the hydrated inorganic phase exhibits only a limited mass loss at 450 °C, ascribed to

the dehydration of  $\text{Ca}(\text{OH})_2$ , whereas the anhydrous cement phase does not show any mass loss [20]. It is noted that the ratio of the mass loss of the first degradation stage to the mass loss of the second degradation stage depends on the foam formulation. This ratio is equal to 0.67 for neat-PUR foam and does not depend on the heating rates; for P-C and HIRP-C foams the same ratio assumes values in the range from 0.8 to 1.1 depending on the heating rate. This result confirms that, in the P-C and HIRP-C foams, the thermo-oxidative degradation of PUR phase occurs with a modified mechanism compared to the neat-PUR. In fact the first degradation steps of anhydrous and hydrated cement composite foams are clearly composed two different processes. The DTG curves show the symmetrical band related to the first degradation step for the neat-PUR comprise the overlapping of two distinct bands for the composites foams. As also reported in papers focused on the effect of clays and organo-modified clay embedded in PUR matrix [29,30], it is likely that the presence of both anhydrous silicate particles and hydrated co-continuous morphology promote the pyrolysis process, in turn allowing, during the first degradation step, for an increased removal of organic matter as volatile pyrolyzed products. More specific studies should be performed to highlight a complete understanding of the chemical mechanisms occurring during the PUR degradation in presence of anhydrous and hydrated cement phases.

Finally the third step at 550–700 °C can be ascribed to the decarboxylation of carbonates phases in both anhydrous and hydrated cement phases.

Table 1 summarizes the thermal degradation data in terms of onset temperature,  $T_d$ , the temperature at the maximum weight loss rate,  $T_{dm}$ , and the weight loss rate,  $d\alpha/dT$  for neat-PUR, P-C and HIRP-C foams at different heating rate, for the several stages identified by TGA.

As it can be observed,  $T_d$  and  $T_{dm}$ , increase as the heating rate increases, whereas the  $d\alpha/dT$  slightly changes with the heating rate; in particular, since  $(d\alpha/dT)_{m3}$  is invariant with respect to heating rate, it is deduced that the third stage of the thermo-oxidative process only concerns the inorganic phase. The residue at 800 °C does not clearly depend on the heating rate. Moreover, the HIRP-C samples showed a residue which is slightly lower than P-C likely due to the presence of calcium hydroxide produced by the hydration of the calcium silicate.

The data of TGA were modeled by Invariant Kinetic Parameters (IKP) method [31], in order to get a better understanding of the phenomena occurring during the thermo-oxidative degradation of neat-PUR, P-C and HIRP-C foams. In particular, the approach is able to calculate the activation energies and the nature of the thermo-oxidative process (i.e. single-step or complex process).

In the IKP method, the kinetic equation for solid decomposition can be expressed as [31,32]:

$$d\alpha/dt = k(T) \cdot f(\alpha) \quad (1)$$

where  $k$  is the reaction constant (i.e. according to the Arrhenius law,  $k = A \exp(-E_a/RT)$ , with  $E_a$  being the activation energy,  $R$  the gas constant and  $A$  the pre-exponential factor),  $\alpha$  (Conversion degree) is the ratio between the weight loss of the foam undergoing degradation at time  $t$  and the total weight loss of the foam in the first degradation step, and  $f(\alpha)$  depends on the particular degradation mechanism. Reformulating Eq. (1) by taking into account the heating rate,  $\beta = dT/dt$  the differential form of the reaction rate under constant conversion becomes:

$$\beta \cdot (d\alpha/dT)_\alpha = A \cdot f(\alpha) \cdot \exp(-E_a/RT) \quad (2)$$

According to the Friedman's method, for which it is not necessary to know the reaction kinetic model, it is possible, from the

**Table 1**  
Thermal degradation data for neat-PUR, composite P–C and hydrated composite HIRP–C foams at varying heating rate.

	Heating rate, (°C/min)	$T_{d1}$ (°C)	$T_{dm1}$ (°C)	$T_{dm2}$ (°C)	$T_{dm3}$ (°C)	$(d\alpha/dT)_{m1}$ (%/°C)	$(d\alpha/dT)_{m2}$ (%/°C)	$(d\alpha/dT)_{m3}$ (%/°C)	Residue at 800 °C, (%wt)
neat-PUR	5	272	310	528	–	0.43	0.67	–	0.6
	10	285	324	558	–	0.43	0.54	–	0.6
	20	294	337	583	–	0.44	0.44	–	1.0
P–C	5	289	318	484	637	0.25	0.60	0.09	56.2
	10	292	325	500	668	0.22	0.59	0.08	57.3
	20	311	344	538	676	0.27	0.56	0.09	56.1
HIRP–C	5	289	313	483	626	0.25	0.56	0.09	55.8
	10	300	326	509	647	0.25	0.65	0.09	55.6
	20	310	345	539	679	0.26	0.55	0.09	55.6

The indexes 1, 2 and 3 point respectively to the first and second stage of PUR thermal degradation and the decomposition of carbonate filler present in the cement mixture.  $T_d$  and  $T_{dm}$  are respectively the onset degradation temperature and the temperature corresponding to the maximum weight loss rate. The term  $(d\alpha/dT)$  refers to the weight loss rate.

slope of the straight line of  $\log[\beta \cdot (d\alpha/dT)]$  versus  $1/T$ , to obtain the activation energy at a certain mass loss  $\alpha$  [30].

In Fig. 5, the energies profile curves over the conversion degree ( $E_a$  versus  $\alpha$ ) corresponding to the first degradation stage (i.e. pyrolysis) for neat-PUR, P–C and HIRP–C foams, are shown. In the range of  $\alpha$  between 0.2 and 0.7, the neat-PUR foam exhibits the invariance (i.e. the changes are less than 10%) of  $E_a$ . This means that the degradation occurs through a single-step process. The activation energy tends to increase at higher  $\alpha$  values ( $>0.7$ ) as a sign of the occurrence of a complex multi-step process. Since the first degradation step of PUR is recognized as a simple single step controlled by pyrolysis mechanism [33], the rise of  $E_a$  at high  $\alpha$  values should be ascribed to the overlapping of physical-controlled (i.e. diffusion of volatile decomposition products) to the chemical-controlled kinetics i.e. degradation of the PUR network through scission of the urethane linkages, degradation of polyols to give ether, ester and water, tri and dimerization of the isocyanate [34,6]. For P–C and HIRP–C foams the activation energy was found to be constant in a limited range of  $\alpha$  values ( $\alpha < 0.4$ ) and, then, it increases monotonically as a sign of the occurrence of a complex multi-steps degradation process, where physical step superimpose to chemicals steps. The finding that the multi-complex degradation process starts at lower conversion in comparison to the neat-PUR foam can be ascribed to the presence of the anhydrous cement and hydrated co-continuous inorganic network, which alters the chemical mechanism of PUR degradation and likely hinders the removal of volatile decomposition products. Moreover, the HIRP–C foam exhibits, all over the  $\alpha$  range investigated,  $E_a$  values higher than those of the neat-PUR and P–C, indicating that the co-continuous morphology due to hydration of the

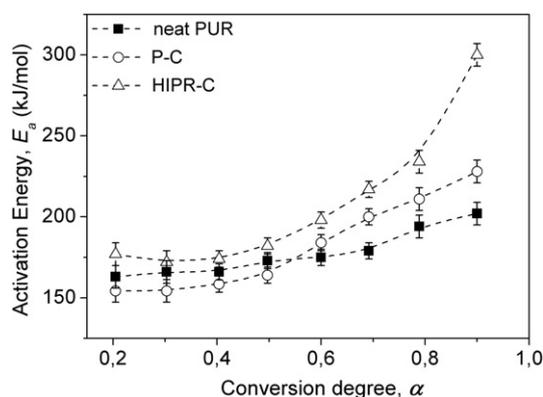
cement particles delays the chain scission (i.e. pyrolysis) and removal of the volatile decomposition products.

To highlight the effect of the co-continuous morphology, which hinders the pyrolysis degradation step owing to its specific structure, TGA data were used to calculate the activation energy values for the HIRP–C reduced as powder by milling. The main scope of this process was to destroy the co-continuous structure and minimize its physical effect. In Fig. 6, the energy profiles over the conversion degree for HIRP–C as foam and powder form are shown.

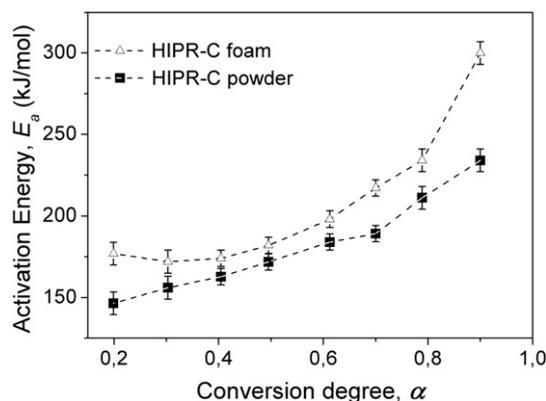
It is noted that the average activation energy values for HIRP–C powder form is lower than those of the HIRP–C foam, confirming that the presence of the continuous inorganic structure contributes to the enhancement of the thermal-oxidative stabilization of the material. However, the energy profile for the HIRP–C powder changes linearly with  $\alpha$ , confirming that the degradation mechanisms that take place are complexes and numerous, over the degradation of the material. Instead, the energy profile for the HIRP–C foam is invariant in respect of  $\alpha$  (up to 0.4), that means a simple single-step process occurs, while, at high  $\alpha$  ( $>0.4$ ) the energy profile changes linearly, sign of the occurring of multi-step mechanisms.

### 3.4.2. Fire resistance

The fire properties of neat-PUR, PUR-FR, P–C and HIRP–C foams were assessed by cone calorimetry. The results in terms of HRR, TTI, pHRR, THR, total mass loss, the smoke production and CO production are summarized in Table 2. All of the values are read directly from the summary test report sheet produced by the cone calorimeter device.



**Fig. 5.** Activation energy,  $E_a$ , results computed by Friedman's method for neat-PUR, P–C and HIRP–C foams.



**Fig. 6.** Activation energy,  $E_a$ , results computed by Friedman's method for HIRP–C in foam and in powder form.

**Table 2**  
Cone calorimeter results.

Sample	TTI (s)	$t_{\text{HRR}}^1$ (s)	$t_{\text{HRR}}^2$ (s)	pHRR (kW/m <sup>2</sup> )	$\Delta$ pHRR %	HRR-average (at 60 s) (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	Total mass lost (%)
Neat-PUR	3	30	62	543	–	364 ± 3	62	80
PUR-FR	5	20	100	448	–17	342 ± 2	50	60
P–C	8	21	184	316	–42	257 ± 3	68	55
HIRP–C	10	21	200	298	–45	201 ± 2	48	37

3.4.2.1. *Heat release rate.* Fig. 7 reports the HRR curves as a function of time for neat-PUR, PUR-FR, P–C and HIRP–C foams. In the inset graph an enlargement of HRR curve at short ignition time is reported.

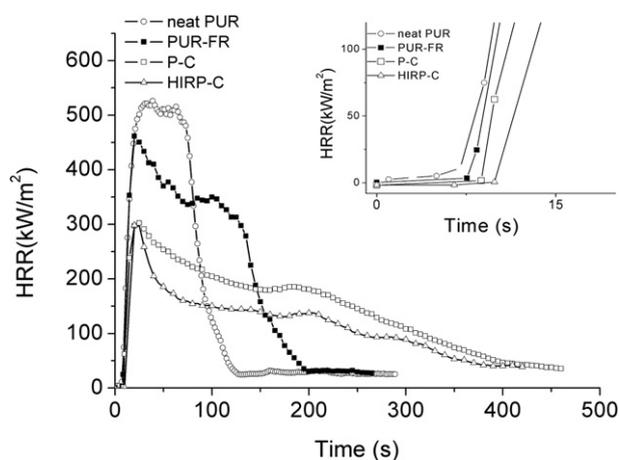
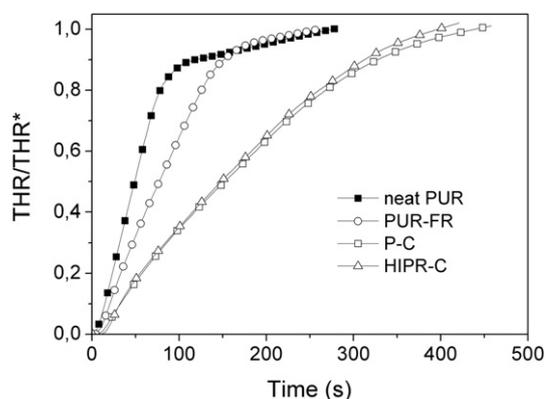
According to the literature related to flame test of polyurethane [2,35], averaged HRR curves for neat-PUR and PUR-FR foams show the typical pyrolysis process and burning of PUR foam under cone calorimeter analysis, consisting of the thermally thick charring (residue forming) step in which an initial peak (attributed to the surface pyrolysis of the foam) appears until the formation of a char layer. Afterwards, due to the continuous heating, the layer char cracks and starts to burn, giving rise to the formation of a second HRR maximum with a suddenly subsequent decrement [2]. In the case of PUR-FR, the presence of the TCPP flame retardant shifts the second HRR peak from around 75 s for the neat-PUR to approximately 125 s for PUR-FR foams. Likely, the TCPP in the foam promotes the formation of a more resistant and stable char layer, which protects the organic matter for successive thermal-oxidative degradation for longer periods. The HRR curves for P–C and HIRP–C foams again show a degradation mechanism characterized by two peaks with the second one at approximately 200 s. The presence of the large amount of the cement phase both as anhydrous particles and as a co-continuous inorganic network acts as a protective layer which delays the subsequent thermo-oxidative decomposition of the organic phase through a reduction of both oxygen absorption and permeation of volatile compounds, respectively, towards and from the surface of the ignited materials. By comparing the HRR curve of neat-PUR with the fire curves of PUR-FR, P–C and HIRP–C, it is possible to observe a broadening of the thermal-oxidative degradation process and decrease of the corresponding curve heights (pHRR), which are associated to enhancements of the fire retardancy property. The flame out is increased to larger values, from 250 s for the neat-PUR and PUR-FR to 450 s for the P–C and HIRP–C. Furthermore the HRR curves (data reported in Table 2) show a reduction of HRR-average (with a maximum change from

364 kW/m<sup>2</sup> for neat-PUR to 201 kW/m<sup>2</sup> for HIRP–C) and a decrease of the pHRR (with a maximum change from 543 kW/m<sup>2</sup> for neat-PUR to 298 kW/m<sup>2</sup> for HIRP–C).

The THR curves, shown in Fig. 8, clarify the effect of TCPP flame retardant and cement phase both as anhydrous and hydrated on the fire degradation kinetics values, reported up to a burn time corresponding to the complete materials degradation (i.e. the time for the lowest HRR values). The THR values have been normalized with the value at the end of the degradation process (see Table 2) to account for the different densities. The presence of large amount of inorganic phase both as anhydrous particles and co-continuous structure slows down the kinetics of the THR. After 100 s of exposure at a 50 kW/m<sup>2</sup> heat flux, the neat-PUR foams has released almost 90% of THR, whereas the PUR-FR releases approximately the 65% and P–C and HIRP–C foams release around 35%. These results confirm that the inorganic phase prevents the heat transfer and the flame spread, therefore protecting the underlying material from further burning.

The TTI for neat-PUR and PUR-FR foams was equal, respectively to 3 and 5 s and, these values are comparable to the results found in the literature for PUR foams, being very low because of the cellular structure of the material [16]. The addition of large amount of cement powder as well as the formation of a co-continuous morphology through cement hydration slightly increases the TTI, which becomes equal to 8 and 10 s for P–C and HIRP–C foams respectively. The TTI increment is mainly ascribed to the higher density and compactness of the P–C (density of 300 kg/m<sup>3</sup>) and HIRP–C (density of 320 kg/m<sup>3</sup>) compared to the densities of neat-PUR and PUR-FR foams (respectively equal to 120 kg/m<sup>3</sup> and 150 kg/m<sup>3</sup>).

The total mass loss or, equivalently, the residue yield seems to depend on the density of the materials. In effect the residue yield of HIRP–C foams of 60 wt% ca well agrees with the TGA residue value at 800 °C. The residues of neat-PUR and P–C foams are respectively slightly higher and lower than those expected on the basis of TGA data. The results confirm that the co-continuous phase promotes

**Fig. 7.** HRR curves of neat-PUR, PUR-FR, P–C and HIRP–C foams.**Fig. 8.** THR values normalized to the THR at end-degradation (THR\*) for neat-PUR, PUR-FR, P–C and HIRP–C foams.

a better combustion of the char formed in the first degradation step, likely ascribed to a more discontinuous phase generated by the hindering effect of the inorganic network. In the case of the P–C foams, the residue is reduced because of the loss of cement particles during the burning process. Hydrated cement phases such as calcium silicate hydrated, calcium hydroxide and hydrated sulfoaluminates (i.e. ettringite) therefore enhances the thermal-oxidative stabilization of PUR foam, resulting in higher thermal stability (slower heat release).

The described can be tentatively associated to the following processes:

- 1) The hydrated cement phases form the co-continuous morphology and act as a protective layer and as a char layer producer, that reduces the oxygen absorption and the removal of volatile decomposition products.
- 2) The co-continuous inorganic structure acts as an internal rigid frame that limits the shrinkage of the foam and allows to be heat internally transferred at longer timer with respect to than those characteristic of neat-PUR and PUR-FR foams.
- 3) The hydrated cement phases (i.e. hydrated calcium silicate, CSH, calcium hydroxide and ettringite) absorb heat by losing water during the decomposition process, with a mechanism similar to the one exerted by flame retardant fillers based on inorganic hydroxide ( $\text{Al}(\text{OH})_3$ ,  $\text{Mg}(\text{OH})_2$ ) [36].

**3.4.2.2. Fire hazard.** The THR and the fire performance index (pHRR/TTI) are important parameters for the definition of the safety ranking of the material. In order to give an ample assessment of the fire hazard, according to Petrella [24] and Babrauskas et al. [37,38], the *flashover* potential can be evaluated by plotting THE values versus pHRR/TTI values [39]. The main reason being that a short TTI and a high peak value of HRR are thought to be necessary requirements for *flashover* to occur. On this basis, the higher the value of pHRR/TTI, the greater the propensity for flashover to occur and the lower the safety rank of the material.

In Fig. 9, the THR values are reported as function of the pHRR/TTI values for the different foams.

The pHRR/TTI values of neat-PUR and PUR-FR (i.e.  $181 \text{ kW/m}^2 \text{ s}$  and  $90 \text{ kW/m}^2 \text{ s}$  respectively) were higher than those of the cement-containing foams (i.e.  $31 \text{ kW/m}^2 \text{ s}$  for P–C and  $29 \text{ kW/m}^2 \text{ s}$  for HIRP–C). This indicates that both neat-PUR and PUR-FR foams exhibit a higher sensitivity to flashover [24,36–38]. Meanwhile the THE values do not significantly change for the neat-PUR, PUR-FR and P–C but, instead decreased remarkably for the HIRP–C foam.

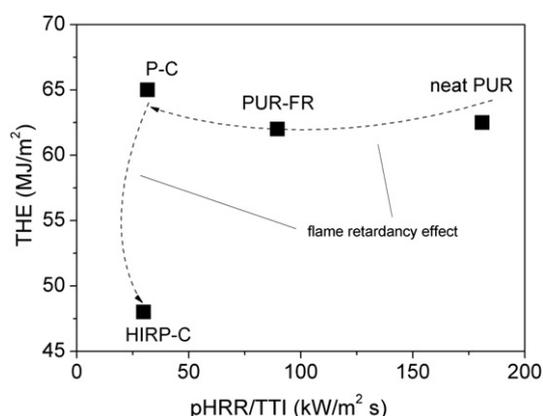


Fig. 9. Flashover potential, pHRR/TTI and HRR for analyzed foams.

It is possible to conclude that, by analyzing the results by the Petrella approach, a slight flame retardancy effect (and, consequently, the reduction of fire hazard) can be ascribed to the use of flame retardants, which mainly affects the fire performance index. Conversely in presence of the co-continuous inorganic structure HIRP–C, a more significant reduction of fire hazard of the PUR matrix was observed, since both pHRR/TTI and THE parameters simultaneously reduced.

Accordingly N. Usta [5], who analyzed the synergistic effect of intumescent flame retardant and fly ash (silico–aluminate filler similar to cement) on rigid PUR foam observed an enhancement of flame resistance behavior in terms of concomitant reduction of pHRR/TTI and THR parameters.

**3.4.2.3. CO production.** It is well-known that most of the fire-related human deaths result from smoke inhalation. Thus, it is important to evaluate the smoke amount, mainly in terms of carbon monoxide, produced during the burning by cone calorimeter of the different materials under evaluation.

The curves related to the amount of emitted CO normalized by the sample weight, are reported in Fig. 10. As it can be observed, the PUR-FR, the P–C and the HIRP–C show a considerable reduction of CO emission with respect to the neat-PUR. This is ascribed to the reduction of the combustible material contained in the foam.

These results confirm that both P–C and HIRP–C affect the degradation mechanism of PUR. In order to have a better understanding of the chemical mechanism involved during burning of PUR phase, the values of CO emission have been normalized to PUR content (combusting matter) to take into account the very different density and composition of the different samples (see the inset in Fig. 10).

The emitted CO per PUR content curves of P–C and HIRP–C are very similar but different with respect to those of neat-PUR and PUR-FR. In particular the results highlighted that the use of cement in the polyurethane formulation allowed for a 18% ca. reduction of the maximum CO evolution rate, with respect to the neat-PUR; while the PUR-FR, in which the FR is specifically designed to reduce the CO emission rate, showed a 48% ca. reduction of the CO peak with respect to neat-PUR. Moreover for neat-PUR foam there is a large emission of CO gas within 100 s, where a depletion of the burning process is observed. The same behavior is evidenced by the PUR-FR foam, although the emission of CO gas occurs within 150 s and the maximum peak is markedly lower than peak for neat-PUR.

Conversely, in the case of both P–C and HIRP–C the emission of CO occurs gradually over the burning process and, at 300 s, is still higher than that of neat-PUR and PUR-FR. The results for PUR foam

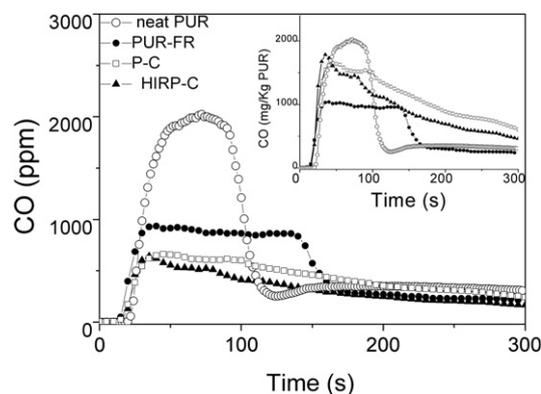


Fig. 10. CO emissions and emitted CO normalized for PUR content of neat-PUR, PUR-FR, P–C and HIRP–C foams.

show that, after a strong emission of CO, the smoldering effect becomes significant, with a level of emission around 400 mg/kg PUR, whereas for P–C and HIRP–C the smoldering effect is delayed.

This means that, for both neat-PUR and PUR-FR foams, the smoldering combustion is fairly important at longer burning times, whereas for the P–C and HIRP–C foams the smoldering effect is obtained only at longer times, where the inorganic cement phases both as free particles and as co-continuous hydrated network are able to further minimize the effect of smoldering combustion.

Finally, the different trend of normalized CO emission curves of P–C and HIRP–C foams, compared to the neat-PUR and PUR-FR, is ascribed to the modified degradation mechanism induced by the presence of cement filler as also observed in the TGA analyses.

#### 4. Conclusions

This work was carried out to establish whether and how the occurrence of hydration of anhydrous cement particles dispersed within a PUR matrix, can lead to improvements in thermal stability and fire resistance of PUR rigid foams. The occurrence of cement hydration, proved by X-ray diffraction and microscopy, accounts for the improvement of mechanical properties in terms of elastic moduli and compressive strength, which increase, respectively, of about 100% and 25% in comparison to neat-PUR foams. The results of thermal characterization obtained by thermogravimetric analysis and cone calorimetric tests on neat-PUR and composite and the hybrid foams showed that the presence of both high amounts of anhydrous cement particles and co-continuous network of hydrated cement phases act as a physical barrier, which delay the transport of oxygen and volatiles, thereby improving the fire behavior of materials. However it is not possible to exclude other mechanisms which may arise from the presence of cement particles, which participate in modifying the conventional degradation process of PUR.

In conclusion, the presence of a co-continuous structure is responsible for the significant improvement in mechanical and functional properties of composite foams, results in an effective delay of the onset of rapid thermo-oxidative degradation and improves the fire resistance of the materials.

#### Acknowledgments

We thank Fabio Docimo for technical support in the preparation of samples and IMAST-High Tech District on Polymeric and Composite Materials Engineering and Structures of Naples, Italy for technical support in the cone calorimetric tests.

#### References

- [1] Bashirzadeh R, Gharehbaghi A. An investigations on reactivity, mechanical and fire properties of PU flexible foam. *J Cell Plastics* 2010;46:129–58.
- [2] Lefebvre J, Bastin B, Le Bras M, Duquesne S, Palejia R, Delobel R. Thermal stability and fire properties of conventional flexible polyurethane foam formulation. *Polym Degrad Stab* 2005;88:28–34.
- [3] Hesheng X, Mo S. Preparation and characterization of polyurethane grafted single-walled carbon nanotubes and derived polyurethane nanocomposites. *J Mater Chem* 2006;16:1843–51.
- [4] Zhang J, Li L, Chen G, Wee P. Influence of iron content on thermal stability of magnetic polyurethane foams. *Polym Degrad Stab* 2009;94:246–52.
- [5] Usta N. Investigation of fire behaviour of rigid polyurethane foams containing fly ash and intumescent flame retardant by using a cone calorimeter. *J Appl Polym Sci* 2012;124:3372–82.
- [6] Singh H, Jain AK. Ignition, combustion, toxicity, and fire retardancy of polyurethane foams: a comprehensive review. *J Appl Polym Sci* 2009;111:1115–43.
- [7] Chen L, Wang YZ. A review on flame retardant technology in China. Part I: development of flame retardants. *Polym Adv Technol* 2010;21:1–26.
- [8] Levchik SV, Weil ED. A review of recent progress in phosphorus-based flame retardants. *Fire Sci* 2006;24:345–64.
- [9] Laoutif F, Bonnaud L, Alexandre M, Lopez-Cuesta JM, Dubois Ph. New prospects in flame retardant polymer materials: from fundamentals to nanocomposites. *Mater Sci Eng R* 2009;63:100–25.
- [10] Berta M, Lindsay C, Pans G, Camino G. Effect of chemical structure on combustion and thermal behaviour of polyurethane elastomer layered silicate nanocomposites. *Polym Degrad Stab* 2006;91:1179–91.
- [11] Seo WJ, Sung YT, Kim SB, Lee YB, Choe KH, Choe SH, et al. Effects of ultrasound on the synthesis and properties of polyurethane foam/clay nanocomposites. *J Appl Polym Sci* 2006;102:3764–73.
- [12] Mahfuz H, Rangari VK, Islam MS, Jeelani S. Fabrication, synthesis and mechanical characterization of nanoparticles infused polyurethane foams. *Compos Part A* 2004;35:453–60.
- [13] Gilman JW. Proceedings of pollution prevention through nanotechnology conference. September 25–26, 2007, Arlington; 2007.
- [14] Zammarano M, Kramer RH, Harris RH, Ohlemiller TJ, Shields JR, Rahatekar SS. Flammability reduction of flexible polyurethane foams via carbon nanofiber network formation. *Polym Adv Technol* 2008;19:588–95.
- [15] Mascia L. Functional fillers for plastics; 2005.
- [16] Modesti M, Lorenzetti A, Besco S, Hrelja D, Semenzato S, Bertani R, et al. Synergism between flame retardant and modified layered silicate on thermal stability and fire behavior of polyurethane nanocomposite foams. *Polym Degrad Stab* 2008;93:2166–71.
- [17] Zatorski W, Brzozowski ZK, Kolbrechi A. New development in chemical modification of fire-safe rigid polyurethane foams. *Polym Degrad Stab* 2008; 93:2071–6.
- [18] Verdolotti L, Di Maio E, Lavorgna M, Iannace S. Foamed polymer-inorganic binder hybrid material having controller density and morphology, method for its preparation and uses thereof. WO2008/007187.
- [19] Verdolotti L, Di Maio E, Lavorgna M, Iannace S. Polyurethane–cement-based foams: characterization and potential uses. *J Appl Polym Sci* 2008;107:1–8.
- [20] Verdolotti L, Di Maio E, Lavorgna M, Iannace S. Hydration-induced reinforcement of rigid polyurethane–cement foams: mechanical and functional properties. *J Mater Sci* 2012;47:6948–57.
- [21] ISO 5660-1. Reaction-to-fire tests – heat release, smoke production and mass loss rate – part 1: heat release rate (cone calorimeter method). 2nd ed. International Organization for Standardization; 2002.
- [22] Bourbigot S, Samyn F, Turf T, Dusquense S. Nanomorphology and reaction to fire of polyurethane and polyamide nanocomposites containing flame retardants. *Polym Degrad Stab* 2010;95:320–6.
- [23] ISO 554. Standard atmospheres for conditioning and/or testing – specifications.
- [24] Petrella RV. The assessment of full-scale fire hazards from cone calorimeter data. *J Fire Sci* 1994;12:15–43.
- [25] Verdolotti L, Di Maio E, Forte G, Lavorgna M, Iannace S. Hydration induced reinforcement of polyurethane foams modified with Portland cement: solvent resistance and mechanical properties. *J Mater Sci* 2010;45:3388–91.
- [26] Taylor HFW. 2nd ed. Cement chemistry. London: Thomas Telford.
- [27] Caputo D, Liguori B, Colella C. Some advances in understanding the pozzolanic activity of zeolites: the effect of zeolite structure. *Cem Concr Compos* 2008; 30:455–62.
- [28] Thirumal M, Khashtgir D, Nando GB, Naik YP, Singha NK. Halogen free-flame retardant rigid polyurethane foam effect of melamine compounds on mechanical, thermal and flame retardancy. *Polym Degrad Stab* 2010;95: 1138–45.
- [29] Song L, Hu Y, Tang Y, Zhang R, Chen Z, Fan W. Study on the properties of flame retardant polyurethane/organoclay nanocomposite. *Polym Degrad Stab* 2005; 87:111–6.
- [30] Xie W, Gao ZM, Pan WP, Hunter D. Thermal degradation chemistry of alkyl quaternary ammonium montmorillonite. *Chem Mater* 2001;13:2979–90.
- [31] Vlase T, Doca N, Vlase G, Bolcu C, Borcan F. Kinetics of non-isothermal decomposition of fire three organox-type antioxidants. *J Therm Anal Calorim* 2008;92(1):15–8.
- [32] De Fenzo A, Formicola C, Antonucci V, Zarrelli M, Giordano M. Effects of zinc-based flame retardants on the degradation behaviour of an aerospace epoxy matrix. *Polym Degrad Stab* 2009;94:1354–63.
- [33] Li XB, Cao HB, Zhang Y. Thermal degradation kinetics of rigid polyurethane foams blown with water. *J Appl Polym Sci* 2006;102:4149–56.
- [34] Camino G, Duquesne S, Delobel R, Eling B. In: Wilkie CA, Nelson GL, editors. Fire and polymers. Washington: ACS; 2001. Symposium Series No 797.
- [35] Prasad K, Kramer R, Marsh N, Nyden M, Ohlemiller T, Zammarano M. Numerical simulation of fire spread on polyurethane foam slabs. *Polym Test* 2009;28:511–20.
- [36] Zhang J, Wang X, Zhang F, Horrocks AR. Estimation of heat release rate for polymer-filler composites by cone calorimetry. *Polym Test* 2004;23:225–30.
- [37] Babrauskas V, Peacock RD. Heat release rate: the single most important variable in fire hazard. *Fire Saf J* 1992;18:255–72.
- [38] Babrauskas V, Peacock RD, Reneke PA. Defining flashover for fire hazard calculations: part II. *Fire Saf J* 2003;38:613–22.
- [39] Scharfel B, Hull TR. Development of fire retarded materials. *Fire Mater* 2007; 31:327–54.